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Enhancement of voltammetric determination of quinizarine based on the adsorption at surfactant-adsorbed-layer in disposable electrodes

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HIGHLIGHTS

- Surfactant-adsorbed-layer in disposable electrodes as antifouling ability.
- Surfactant-adsorbed-layer: a simple approach to improve electroanalysis of dye marker.
- Cationic surfactant enables minimizing matrix effects of commercial fuel.

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ABSTRACT

Screen-printed carbon electrode (SPCE) surface was easily altered through spontaneous hydrophobic interactions with cationic surfactant cetyltrimethylammonium bromide (CTAB) to form a surfactant-adsorbed-layer. This finding combined the practicality of the SPCE with the CTAB's anti-fouling ability and preconcentration properties as a suitable alternative to determine the quinizarine in fuel samples using the square-wave voltammetric technique. Under optimized experimental conditions the electroanalytical method presented a linear response from 5.00×10^{-7} to 6.00×10^{-6} mol L^{-1} ($r = 0.998$) with a detection limit of 2.70×10^{-7} mol L^{-1}. The methodology was successfully applied in the dye marker quantification in diesel oil and kerosene samples, without matrix interference, with recoveries values highly satisfactory and ranged between 84.0% and 98.7%.

1. Introduction

Nowadays, it is not possible to discuss motor vehicles without considering air quality standards, in which the vehicles have a great impact due to its pollutants emissions, such as nitrous oxide (NOx) and sulfur compounds. Therefore, the reduction and control of the composition and quality of these fossil fuels have played a great role recently [1–5]. The guarantee of these products is usually associated with the use of dyes and/or markers aiming to protect the source, destination and possible fuel adulterations [3–9].

In this context, the 1,10-dihydroxyanthraquinone, also called quinizarine (QNZ), Fig. 1, is one of the anthraquinone dyes commonly used as fuel marker to distinguish the origin and quality of fuels [3,5]. This practice is important and spread throughout the world and the fuels are taxed according to government rates, which depend on the types as well as on their application purposes [3–8].

For instance, the aviation fuels guarantee is obtained through the identification of fuel grades marked with dyes so that it prevents fraud and helps to provide evidences of fuel dilution with solvents [3–8]. The most useful analytical methods adapted to control this adulteration are based on the control of these dyes by using espectrofotometric [10], liquid chromatographic [11–15] and electroanalytical methods [16–19]. However, the evaluation of the fuel samples requires a very sensitive detection system due to the problem concerning the dilution with hydrocarbon solvents, in which different kinds of mixture can be found. Spectrophotometry [10] and liquid chromatographic techniques coupled with UV–VIS, UV–VIS-DAD [11–14] and mass spectrometry [20] detectors have been more efficiently employed for this purpose. In addition, liquid chromatographic techniques coupled with electrochemical detection were also developed to determine a mixture of dyes in gasoline and ethanol samples after a simple and fast pretreatment protocol [21–23]. Nevertheless, electroanalytical techniques have also been explored for the detection and determination of markers in different fuels samples such as ethanol, kerosene, gasoline and diesel [16–19]. On reported papers, we have

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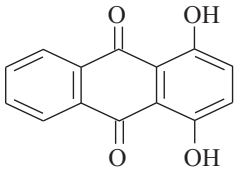

Fig. 1. Chemical structure of quinizarine (QNZ).

shown that the electroanalytical method can be successfully applied to quantify quinizarine [16], Solvent Blue 14 [17] and Solvent Orange 7 [18] in different fuel samples. All the methodologies offer an economical method able to detect and quantify these dyes on glassy carbon electrode surface in a satisfactory concentration level. To improve even more the voltammetric response of their ported method [17], the glassy carbon working electrode was changed by screen-printed carbon electrodes(SPCE) and also used to quantify the dye Solvent Blue 14 in ethanol and kerosene in a concentration level of 2.90×10^{-7} mol L^{-1} [19]. The advantage found in the use of these classes of electrodes was mainly the possibility to explore their portability, simplicity of operation, once the SPCE are small footprint tools, whose arrangement contain, in a simple way, the working electrode and the auxiliary and reference electrodes printed directly onto a polymeric/plastic foil.

Although the electrochemical detection system can be recommended when low-level detection and interference separations are required, the direct application of the voltammetric method to monitor quinizarine is not easy to operate and requires a long step of electrode surface cleaning once adsorption effect is observed during electrochemical process, promoting a voltammetric signal distortion that difficult the construction of an analytical curve with enough accuracy. Therefore, the use of screen-printing carbon electrodes (SPCE) as a tool able to improve the detection of complex analytes is in agreement with the results demonstrated in the literature [24–26]. They consist of a simple dispositive where all the electrodes are printed on a substrate offering an effective electrochemical system that can be commercially implemented as a disposable tool [24–26]. Then, the purpose of the present work was to combine the simplicity of SPCEs with the use of CTAB surfactant as an anti-fouling agent to avoid surface passivation and achieve satisfactory analytical performance, capable of offering a fast and sensitive alternative for the QNZ determination in diesel oil and kerosene samples.

2. Experimental

2.1. Instrumentation

Voltammetric measurements were carried out on an Autolab PGSTAT-30 (ECO-Chemie, Utrecht, The Netherlands) connected to a controlled microcomputer with the General Purpose Electrochemical System (GPES 4.9) software for data acquisition and experimental control. An electrochemical cell with maximum capacity of 10 mL, specially adapted to insert the screen-printed carbon electrode (AC1.W4.RS, BVT-Technologies, Czech Republic) was used for electroanalytical analysis. The design of the screen-printed carbon electrode (SPCE) used in all the electrochemical experiments consists of a ceramic base with 25.4 mm length, 7.26 mm width and 0.63 mm thickness. The abbreviations are represented as follows, AC1:amperometric electrode with corundum ceramic base, W4:working electrode material composed only by graphite, RS: reference electrode material composed by silver. The auxiliary electrode was made out of conducting carbon ink. The SPCE was connected to the potentiostat via a connector cable (model, KA1, BVT-Technologies, Czech Republic) and all the electrodes were used without any pretreatment step.

All pH measurements were carried out in a combined glass electrode (Orion, Thermo Electron Corporation) connected to the digital pH-meter (Orion, Thermo Electron Corporation) and are expressed as $pH_{apparent}$ (pH^*). The deionized water used to prepare the supporting electrolyte and surfactants solutions was purified with a Milli-Q (model Simplicity 185, Millipore) system and had a resistivity of 18 MΩ cm^{-1}.

2.2. Reagents and solutions

Stock solutions of QNZ (Sigma–Aldrich, São Paulo, Brazil) (1.00×10^{-3} and 1.00×10^{-2} mol L^{-1}) were prepared by dissolving the solid product in acetonitrile (J.T. Baker, São Paulo, Brazil). Diluted working standard solutions were then prepared daily with acetonitrile only before their use. The working solutions had shown sufficient stability under a storage period of up to three months (the time of evaluation).

The Britton–Robinson (B–R) (0.08 mol L^{-1}) buffer, with a pH between 2.0 and 9.0, was used in the supporting electrolyte solution composition and conventionally prepared: a mixture containing 0.08 mol L^{-1} of acetic acid, 0.08 mol L^{-1} of boric acid and 0.08 mol L^{-1} of orthophosphoric acid (all Merck, São Paulo, Brazil) with the appropriate amount of 1.0 mol L^{-1} of sodium hydroxide (Merck, Darmstadt, Germany) solution to adjust the pH to the required value. The N,N-dimethylformamide (DMF) (J.T. Baker, São Paulo, Brazil) was used as the organic composition of supporting electrolyte solution in the mixture with B–R buffer solution. The surfactant, cetyltrimethylammonium bromide (Merck, São Paulo, Brazil), was prepared at a concentration of 0.03 mol L^{-1} in deionized water.

Kerosene and diesel fuel samples (collected in Araraquara city, São Paulo, Brazil), after certifying that there was no evidence of the target dye, were spiked with 1.50 and 2.50 mg L^{-1} of QNZ using an appropriate volume of the stock solution.

2.3. Procedure for voltammetric measurements

A 5.0 mL aliquot of the supporting electrolyte (B–R buffer pH 7.0 and DMF, 7:3 v/v) was added to the electrochemical cell (adapted to insert the SPCE) and deoxygenated by purging with pure nitrogen for approximately 15 min to eliminate dissolved oxygen. After that, an aliquot of the surfactant solution (0.03 mol L^{-1}) was added to the cell under stirring for 5 min. The stirring was stopped and after a 15-second rest, cyclic or square-wave voltammograms were registered. After the background voltammogram be recorded, the aliquot of the dye solution was added to the cell and then the voltammogram was recorded for the same screen-printed carbon electrode (SPCE). It was verified that, despite the fact that SPCE are commercialized as disposable electrochemical sensors, the successively recorded voltammograms for QNZ detection in the presence of surfactant solution have shown a negligible change in the cathodic peak for up to 40 repetitions using the same electrode. Therefore, before each series of measurements the SPCE was kept resting for approximately 35 s, enough time to reestablish the surface.

2.4. Analysis of diesel and kerosene samples containing QNZ

The methodology was performed after adaptation of works previously published [16,19]. An aliquot of 1.00 mL (spiked to 2.50 mg L^{-1} of QNZ) and 2.00 mL (spiked to 1.50 mg L^{-1} of QNZ) of aviation kerosene and diesel fuel samples were transferred to a solid-phase extraction (SPE) cartridge containing 0.60 g of silica, previously conditioned with 5.0 mL of hexane. The sample was

slowly forced through the SPE cartridge (flow rate around 2.0 mL min^{-1}), using a syringe attached to the top of the cartridge. After this, the cartridge was washed with approximately 10 mL of hexane to remove all hydrocarbons and contaminants from the matrix. Afterward, the dye was eluted from the cartridge using the mixture containing B–R buffer (pH 7.0) and DMF in the ratio of 7:3 (v/v). The eluent was collected in a 10.0 mL volumetric flask and after the addition of the CTAB surfactant (125 μL of 3.30×10^{-2} mol L^{-1} solution), the volume was completed with the mixture B–R:DMF 7:3 (v/v). The resulting solution was analyzed by using square-wave voltammetric and the quantification of the dye in the sample was performed using the standard addition method.

3. Results and discussion

3.1. Electrochemical behavior of QNZ on the SPCE

Cyclic and square-wave voltammograms were utilized as means to test and compare the effect of surfactants on SPCE in relation to the QNZ reduction in different supporting electrolyte solutions investigated. Among several surfactants tested, the QNZ solubility as well as its detectability was improved only in the presence of the cetyltrimethylammonium bromide (CTAB).

Fig. 2 displays typical cyclic voltammograms obtained for electrochemical reduction of QNZ (5.00×10^{-5} mol L^{-1}) in a mixture of B–R buffer (pH 7.0) and DMF (7:3, v/v) before (Curve B) and after addition of 7.50×10^{-4} mol L^{-1} of CTAB (Curve C). A well-defined cathodic peak is observed at −0.78 V (voltammogram B) and −0.68 V (voltammogram C), respectively, both expressed *versus* silver pseudo-reference from SPCE. The target peak, in both voltammograms, was attributed to the electron-transfer involving the reduction of central quinone group to form hydroquinone derived after a two-electron process, as previously reported in the literature with different working electrodes [16–19,27]. On reverse scan, only in the voltammogram recorded in micellar medium was possible to detect the occurrence of anodic peaks close to −0.65, −0.50 and −0.41 V (*vs.* silver pseudo-reference from SPCE), named as $E_{pa(1c)}$, $E_{pa(2c)}$and $E_{pa(3c)}$, respectively. Based on Zinger's work [27] regarding electrochemistry of quinizarine adsorbed on a glassy carbon electrode in aqueous solutions, we assign these phenomena to the oxidation of the reduced form and/or oxidation involving different species generated after secondary reaction, whose adsorption is not preponderant in the presence of CTBA. For analytical purposes, only the cathodic peak at −0.68 V ($E_{pc(1C)}$, voltammogram C) presented satisfactory analytical performance and was chosen to further studies.

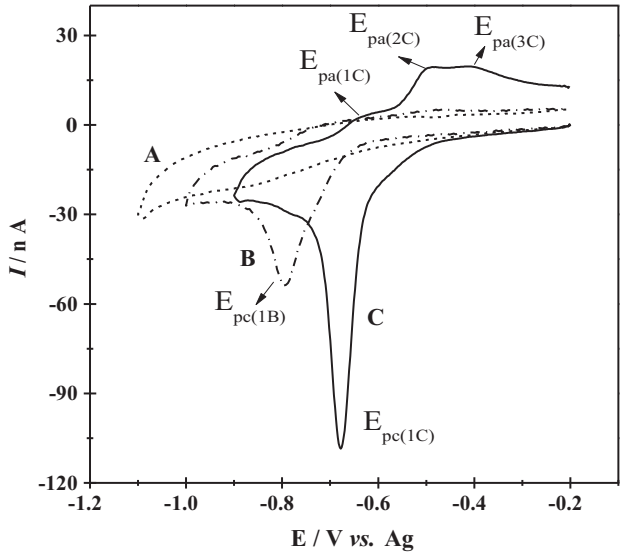

Fig. 2. Cyclic voltammograms indicating electrochemical reduction of QNZ (5.00×10^{-5} mol L^{-1}) on the SPCE surface using 0.080 mol L^{-1} of B–R buffer (pH 7.00) containing 30% of DMF as supporting electrolyte solution. (curve **A**) blank, 0.080 mol L^{-1} of B–R buffer (pH 7.00) containing 30% of DMF and the presence of CTAB (7.50×10^{-4} mol L^{-1}), (curve **B**) reduction of QNZ (5.00×10^{-5} mol L^{-1}) in the absence of CTAB and (curve **C**) reduction of QNZ (5.00×10^{-5} mol L^{-1}) in the presence of CTAB (7.50×10^{-4} mol L^{-1}). Scan rate of 100 mV s^{-1}.

Regarding the reduction peak(relative to the $E_{pc(1C)}$, Fig. 2 – voltammogram C) registered in micellar medium, it is possible to observe that it is narrowed and visibly amplified, which is almost three times higher than the one obtained in the absence of CTAB. Additionally, there was a potential shifting of 100 mV to a less negative region in relation to the voltammogram recorded on the SPCE in the absence of CTAB (Fig. 2, voltammogram B). Except this, no other modification in the voltammetric behavior was observed in all voltammograms recorded for each new electrode, indicating that the use of the CTAB surfactant and SPCE presents suitable conditions to improve the electroanalytical detection of QNZ and could be used for analytical purposes.

According to several studies, it has been recognized that surfactants can spontaneously adsorb on a rough surface, such as carbon paste electrodes (CPEs), carbon nanotubes (CNTs) and SPCEs via hydrophobic interactions to form a surfactant-adsorbed-layer [28–33]. Certainly, the improvement in the voltammetric response should arise from the enhanced adsorption of analyte in surfactant-adsorbed-layer. Thus, the sensitive response of QNZ after addition of CTAB to the electrochemical cell (Fig. 2, voltammogram C) may be related to electrostatic interactions between QNZ and CTAB, leading to an improvement of QNZ accumulated on the electrode surface through the CTAB adsorbed layer. Moreover, the peak current amplification was accomplished with the displacement of the peak potential to the less cathodic region, in the presence of CTAB, which could also be correlated with cationic surfactant interaction on the electrode surface (surfactant-modified surface), acting as an anti-fouling agent and assisting in the electron transfer for the QNZ reduction onto SPCE surface.

Electrode surface poisoning is frequently discussed in literature when cyclic voltammograms are obtained for bare electrode [34–36]. In agreement with these previous reports, we have also found that the peak current registered in different electrode surface [16–18] was noticeably lowered up to disappear after successive potential scanning or during continuous measurements, confirming the existence of electrode-surface-fouling. This behavior was observed even when cleaning the SPCE surface with organic solvent and/or after electrochemical pretreatment before recording the voltammogram. However, in the presence of CTAB, the voltammogram profile could be re-established (about 40 repetitions) after 35 seconds of a rest period before each series of measurements. Thus, the surfactant presents anti-fouling capacity under this experimental condition, improving the viability of the use of SPCE to detect QNZ without adsorption complications.

3.2. Effect of pH

In previous works regarding voltammetric studies of anthraquinone dyes [16–19,23], it was also observed that the pH of supporting electrolyte has a strong influence on the voltammetric behavior and the peak current, as well as peak potential was strongly pH-dependent involving pre-protonation reactions. To test the pH influence, cyclic voltammograms were recorded for electrochemical reduction of QNZ (5.00×10^{-5} mol L^{-1}) in 0.10 mol L^{-1} of B–R buffer containing 30% of DMF and the presence of CTAB

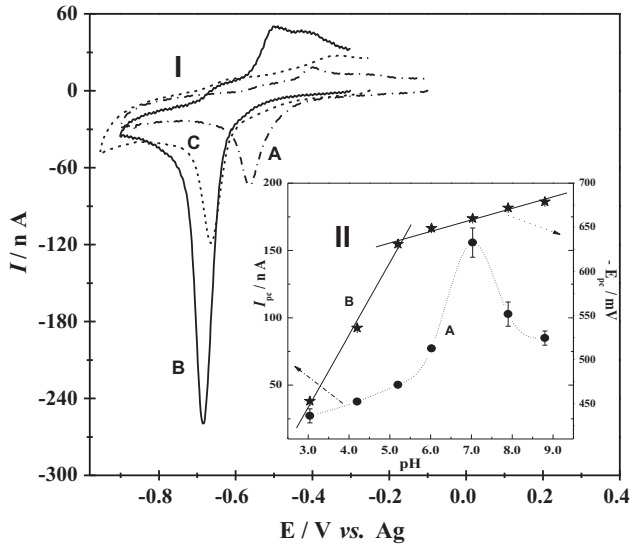

Fig. 3. (I) Cyclic voltammograms registered for the SPCE indicating the electrochemical reduction of QNZ (5.00×10^{-5} mol L^{-1}) in 0.08 mol L^{-1} of B–R buffer containing 30% of DMF and the presence of 7.50×10^{-4} mol L^{-1} of CTAB at: (A) pH 5.2, (B) pH 7.0 and (C) pH 7.9. (II) Inset: Influence of pH on the peak current and peak potential response for the pH range between 3.0 and 8.9. Scan rate of 100 mV s^{-1}.

(7.50×10^{-4} mol L^{-1}) using B–R buffer solution adjusted at pH values from 3.00 to 8.90. Fig. 3(**I**) displays cyclic voltammograms obtained for acidic (Fig. 3**I**, voltammogram (A), neutral (Fig. 3**I**, voltammogram (B) and basic (Fig. 3**I**, voltammogram (C) media. The dye reduction presented analytical peaks with higher intensity in neutral conditions than in acidic and basic media. At pH values higher than 8.90 there is no peak current definition; besides, a considerable shifting to more negative potentials was observed, which overlapped with the supporting electrolyte reduction so that the peak current could not be accurately measured.

Fig. 3II (inset) illustrates the effect of pH on the peak current intensity and the peak potential. The peak current (Fig. 3II) presented an interesting non-linear behavior as a function of pH, wherein the response increases continually as pH increases from 3.00 to 7.00 and the maximum peak current intensity is obtained at this pH value. Between pH 7.00 and 8.90, the peak current intensity decreases considerably and the peak potential appears close to the hydrogen reduction current, losing analytical applicability. These behaviors may indicate that electrostatic interaction and consequently adsorption of QNZ in CTAB-adsorbed-layer occurs preferentially when QNZ ($pKa \cong 9.0$) is in non-ionic form. From the Fig. 3II (inset), the E_p*vs* pH graphs reveal two linear ranges intersecting at pH 5.30 and also show that the peak potential for QNZ reduction is shifted to more negative potentials, demonstrating protonation reactions coupled to the electron transfer [27,37]even in the presence of CTBA. The linear range for $3.00 \leqslant pH \leqslant 5.20$ is represented by the following equation $E_{pc}(V) = 197 - 82 \times pH$ ($r = 0.994$), suggesting that equivalent number of protons and electrons are involved in the reduction process of QNZ [16,17]. In alkaline medium there is a decrease of current intensity, which is an indicative that the hydroxyl groups in QNZ are dissociated and also impedes the interaction with CTAB and/or the adsorption in CTAB-adsorbed-layer. Thus, from electroanalytical viewpoint the apparent pH close to 7.00 was selected as ideal for QNZ detection using this experimental condition, which offered an improved interaction between the dye and the cationic surfactant, and consequently enhancing the analytical applicability.

3.3. Voltammetric studies using square-wave voltammetry (SWV)

In order to enhance the voltammetric response, the effect of the CTAB surfactant on the peak current intensity was studied recording square-wave voltammograms (SWV). The reduction peak of QNZ (5.00×10^{-6} mol L^{-1}) was monitored after changing the CTAB concentration in the electrochemical cell from 5.00×10^{-5} to 1.50×10^{-3} mol L^{-1}. An intense and well-defined reduction peak was observed at around −0.70 V (*versus* silver pseudo-reference from SPCE), whose intensity was practically three times higher than the one produced in the absence of the surfactant. However, the peak current was more pronounced by increasing CTAB concentration up to 1.00×10^{-3} mol L^{-1}, reaching a plateau above these concentrations.

Fig. 4 illustrates typical square-wave voltammograms for reduction of QNZ (4.00×10^{-6} mol L^{-1}) on the SPCE after discrimination of forward current (Fig. 4, curve **a**), backward current (Fig. 4, curve **b**) and resultant current (Fig. 4, curve **c**). This voltammetric behavior shows that QNZ in CTBA medium is reduced following a reversible electron transfer process [38,39]. It is known in the literature that micellar medium can alter the properties of electrode surfaces, including the enhancement of the electron-transfer-rate reactions [28–36]. Accordingly, this voltammetric behavior indicates that the electrochemical reduction of QNZ is facilitated in micellar medium containing CTAB. The results also indicate that up to the critical micellar concentration (CMC) the oriented film on surfactant-adsorbed-layer could facilitate the reduction of QNZ that is close to the electrode due interaction with CTBA by its hydrophilic head. This alignment of QNZ in the CTBA film formed on electrode surface could improve the electron-transfer-rate and consequently decreases the overpotential, which is also important to improve the detectability for determining the target dye.

The use of SWV to record simultaneously the forward and the backward currents, as well as the addition of CTAB surfactant in the electrochemical cell provide evidence that the chemical reaction following the electron transfer is minimized. This hypothesis is reinforced by observing the ratio of both forward and backward currents ($\boldsymbol{I}_{backward}/\boldsymbol{I}_{forward}$)in Fig. 4 (inset), plotted against frequency

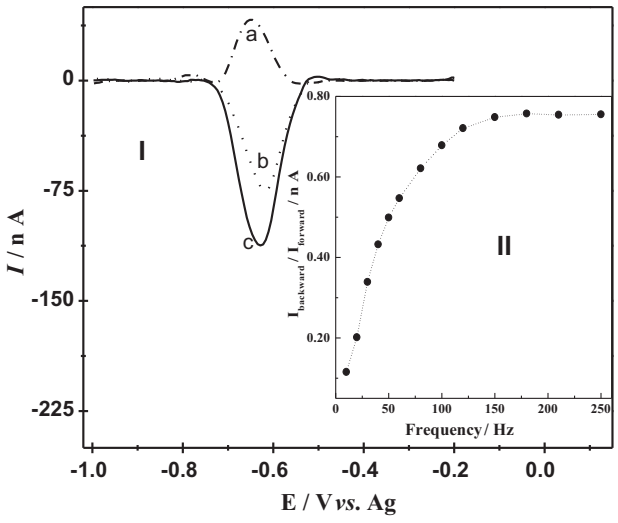

Fig. 4. (I) Square-wave voltammogram indicating electrochemical reduction of QNZ (4.00×10^{-6} mol L^{-1}) registered in supporting electrolyte solution composed by 0.08 mol $L^{-1}$of B–R buffer (pH 7.00) containing 30% of DMF and the presence of CTAB surfactant (7.50×10^{-4} mol L^{-1}). (a) Forward current, (b) backward current and (c) resultant current. Conditions: frequency (f) = 60 Hz, step potential (ΔE_s) = 6 mV and pulse amplitude (E_{sw}) = 25 mV. (**II**) Inset: Variation of the ratio ($\boldsymbol{I}_{backward}/\boldsymbol{I}_{forward}$) versus frequency. Conditions for inset Figure: step potential (ΔE_s) = 2 mV and pulse amplitude (E_{sw}) = 25 mV.

after variation between 10 and 250 Hz. In this case, the relationship clearly suggests that the electron transfer is controlled by a reversible process when the frequency is increased between 10 and150 Hz, reaching a constant value close to the unity from 150 Hz [38,39].

Clearly, the use of the CTAB surfactant has brought many benefits to the QNZ detection onto SPCE, since its presence has tripled peak current values and led to a concomitant negative shift of the peak potential. This feature was not possible when using bare SPCE, and then the reduced QNZ irreversibly adsorbed onto the electrode surface causing the fouling and inactivate one. In the presence of CTAB, the direct contact of electro generated QNZ-product with the electrode was avoided due to QNZ adsorption in CTAB-adsorbed-layer. In fact, when the surfactants concentration is lower than CMC, the monomers behave like independent molecular entities in aqueous medium. However, when the concentration is increased they tend to form aggregates of various sizes [28–31]. The micelles formation can also stabilize the QNZ molecules, hindering its adsorption in CTAB-adsorbed-layer. Hence, the ratio between QNZ and CTAB concentrations is an important parameter to control, so that all the further studies were carried out using a ratio [CTAB]/[QNZ] at around 15/1.

3.4. Analytical curve

As well known, the voltammetric signal on SWV depends highly on the excitation potential and the evaluation of target instrumental parameters, such as frequency (***f***), step potential ($\Delta\mathbf{E_s}$) and pulse amplitude ($\mathbf{E_{sw}}$), which can play an important role in enhancing the detectability and sensitivity of the electrochemical detection system. Thus, to improve the electroanalytical performance of the SWV technique before developing the methodology, the frequency (from 10 to 250 Hz), step potential (from 2 to 12 mV) and pulse amplitude (from 10 to 100 mV) were evaluated, keeping QNZ concentration at 5.00×10^{-6} mol L^{-1}. The adequate working conditions were chosen by evaluating the peak current intensity and voltammetric resolution, and the higher values for the instrumental parameters studied provided very broad peaks. Accordingly, it was observed that $f = 60$ Hz, $\Delta E_s = 6$ mV and $E_{sw} = 50$ mV provided the best voltammetric profile and the peak current intensity was recorded accurately.

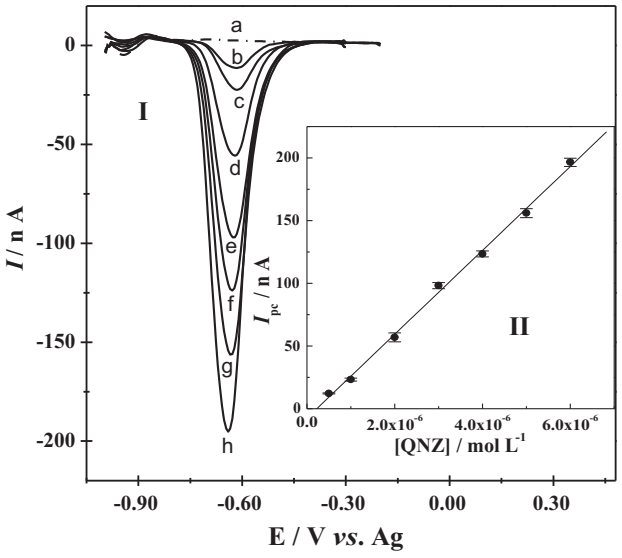

Fig. 5. (I) Square-wave voltammograms indicating electrochemical reduction of QNZ in 0.08 mol L^{-1} of B–R buffer (pH 7.0) with 30% of DMF and the presence of CTAB surfactant (7.50×10^{-4} mol L^{-1}) for increasing concentration as follows: (a) blank, (b) 5.00×10^{-7}, (c) 1.00×10^{-6}, (d) 2.00×10^{-6}, (e) 3.00×10^{-6}, (f) 4.00×10^{-6}, (g) 5.00×10^{-6} e and (h) 6.00×10^{-6} mol L^{-1}. (II) Inset: Analytical calibration function for the dependence of the peak current on the QNZ concentration. Parameters: $f = 60$ Hz, $\Delta E_s = 6$ mV and $E_{sw} = 50$ mV.

The optimized condition was used to detect QNZ at different concentrations in advance to construct the analytical curve. Fig. 5 illustrates the respective voltammograms recorded from 5.00×10^{-7} to 6.00×10^{-6} mol L^{-1} QNZ using the same SPCE and an intermediate step of 35 second of rest before each measurement. In the Fig. 5 (inset), the peak current increased in the entire concentration range studied, and the analytical linear curve accords with the equation $\boldsymbol{I_{pc}}(\text{nA}) = -7.52 + 3.35 \times 10^7 \times \boldsymbol{C}$ (mol L^{-1}), with correlation coefficient $r = 0.998$. The statistical treatment $3 \times \mathbf{Sd}/\boldsymbol{m}$ and $10 \times \mathbf{Sd}/\boldsymbol{m}$ was used to calculate the limits of detection (LOD) and quantification (LOQ), respectively. **Sd** corresponds to the standard deviation for peak current values at $\mathbf{E_p}$ for QNZ reduction, measured from the register of ten voltammograms of the blank and ***m*** is the slope of the analytical curve [40]. Table 1 presents all the parameters values obtained from analytical curve, which were remarkably more satisfactory than those reported for glassy carbon electrode [16]. The analytical parameters obtained were also compared with those obtained by using HPLC method for analyzing QNZ in diesel fuel samples [41] and the proposed method proved to be advantageous, providing similar or higher sensitivity.

3.5. Analytical application

From the employment of the best experimental and instrumental conditions described above, the matrix effects were tested by addition-recovery experiments carried out in fuels samples treated as previously mentioned in the experimental part (Section 2.4). Firstly, the collected fuels samples were tested to confirm the absence of target dye as marker in commercial matrices and then submitted to voltammetric analysis according to standard addition method. The addition-recovery tests were essential to study the interferences caused by hydrocarbons and other components present in the matrix, which can suppress the voltammetric signal. Accordingly, a simple pretreatment procedure with a solid phase extraction (SPE) cartridge column (containing silica) was used (Section 2.4). Fig. 6 illustrates characteristic voltammograms recorded for QNZ determination in the diesel fuel sample after pre-treatment procedure (Fig. 6, line a), as well as its quantification after standard addition (Fig. 6, lines b–e). These square-wave voltammograms reveal those hydrocarbons and others interferences compounds present in diesel fuel sample effectively removed during the pretreatment stage and the well-defined peak presents a satisfactory performance for the analytical purpose. Similarly, the recorded voltammograms obtained for QNZ determination in kerosene fuel (1.50 mg L^{-1} and 2.50 mg L^{-1}, respectively) did not present any matrix effects after using a pretreatment step as described in the experimental procedure (Section 2.4). Table 2 shows the recoveries (ranging from 84.0% to 98.7%) obtained for each analyzed sample, which represent an average of four determinations. All standard addition curves recorded in these analyses presented suitable linearity, with correlation coefficient close to 0.99, demonstrating that QNZ determinations in target samples can be reliably performed.

The key to the methodology development was the use of CTAB surfactant, which is an important part of the strategy to prevent interference from matrix constituents as well as to protect the electrode surface from adsorption of electro generated products. Additionally, comparing these results obtained with those using the reference method [16,41], no significant difference between the reference and the proposed methods was observed. Finally, the obtained data by statistical calculations were satisfactory and

Table 1
Experimental parameters obtained from calibration curve for QNZ detection as in Fig. 5.

Parameters	Proposed method	Reported methods	
		Electroanalytical [16]	Liquid chromatographic [41]
Linear range (mol L^{-1})	(0.50–6.00) $\times 10^{-6}$	(2.00–14.0) $\times 10^{-6}$	(2.00–43.0) $\times 10^{-6}$
Intercept	−7.52[a]	−0.19[b]	NR
Slope	3.35 $\times 10^{7}$[c]	7.20 $\times 10^{5}$[d]	NR
Correlation coefficient (r)	0.998	0.999	NR
LD (mol L^{-1})	2.70 $\times 10^{-7}$	4.10 $\times 10^{-7}$	8.25 $\times 10^{-7}$

Units: [a] = nA; [b] = μA; [c] = nA L mol^{-1} and = [d] = μA L mol^{-1}; NR: not reported.

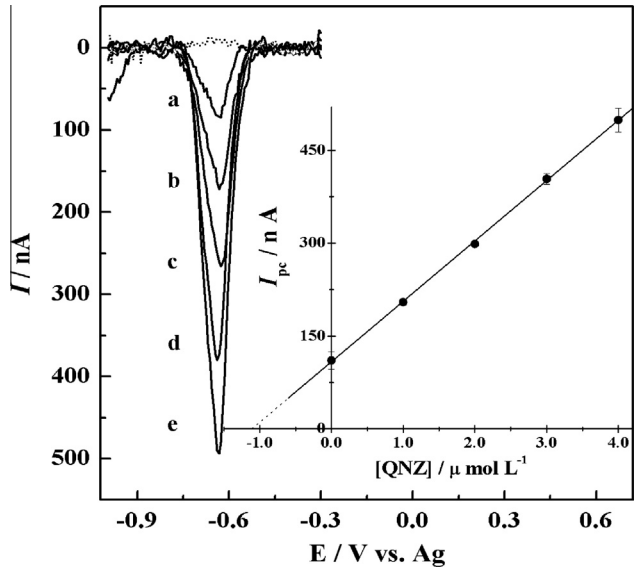

Fig. 6. Square-wave voltammograms obtained for the determination of QNZ in 0.08 mol L^{-1} of B–R buffer (pH 7.0) with 30% of DMF and the presence of CTAB surfactant (7.50 $\times 10^{-4}$ mol L^{-1}). (a) Non-spiked blank, diesel after extraction as described in Section 2.4, (b) 1.00 mL diesel sample containing 2.50 mg L^{-1} of QNZ after extraction procedure as mentioned in Section 2.4, (b–e) successive additions (5.00 μL) of QNZ (1.00 $\times 10^{-3}$ mol L^{-1}). Inset: Analytical calibration function for the dependence of the peak current on the QNZ concentration. Parameters: f = 60 Hz, ΔE_s = 6 mV and E_{sw} = 50 mV.

Table 2
Statistical evaluation for the results obtained regarding electroanalytical determination of QNZ in kerosene and diesel samples.

Samples	Added(mg L^{-1})	Found ± μ (mg L^{-1})[a]	Recovery (%)	RSD (%)
Kerosene	2.50	2.10 ± 0.10	84.0	3.20
Kerosene	1.50	1.48 ± 0.20	98.7	8.70
Diesel	2.50	2.42 ± 0.27	96.8	7.00

[a]Average of four determinations; μ = confidence interval = $\mu = \pm \frac{tSD}{\sqrt{n}}$, where: $t_{critical}$ = 3.18 for confidence level of 95%, SD = standard deviation, n = number of determinations = 4; RSD: relative standard deviation.

compatible to those required for a reliable analytical method, indicating that the proposed method could be applied to the analysis of QNZ in diesel and kerosene fuel samples.

4. Conclusions

In this work, we showed the enhancement of the quinizarine determination based on the use of CTAB to provide improvement in the adsorption of target dye on surfactant-adsorbed-layer in disposable electrodes. The simple alternative of the use of cationic surfactant has also brought improvement in the QNZ detection because of the CTAB ability to act as anti-fouling agent, avoiding electrode passivation from matrix effects and electro generated product on the SPCE surface. This alternative has also allowed to use only one SPCE during each series of determination, when each determination was composed for at least 40 measurements. Furthermore, the use of CTAB was essential to improve the electroanalytical response lowering the detection limit and allowed the determination of the target dye in spiked fuels samples at low concentration levels without matrix interference. Finally, these findings provide more satisfactory results when compared with the previously reported methods [16,41] and offer analytical performance comparable to chromatographic techniques providing an important alternative to the careful control of the final dye concentration in complex fuel samples.

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